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[Claim 1] An alkaline storage battery comprising nickel cathodes and an alkaline electrolytic solution, wherein at least one species of a compound selected from the group consisting of niobium compound, titanium compound, tungsten compound and molybdenum compound is introduced into the nickel cathodes comprising a cathode active material composed mainly of nickel hydroxide, which surface has a coating layer of a cobalt compound, and the alkaline electrolytic solution contains lithium hydroxide, a lithium hydroxide content being not less than 0.6 mol / L and not more than 1.6 mol / L.

[Claim 2] An alkaline storage battery according to claim 1, wherein the cobalt compound is a cobalt compound containing alkali metal ion.

[Claim 3] An alkaline storage battery according to claim 1, wherein the amount of at least one species of a compound selected from the group consisting of niobium compound, titanium compound, tungsten compound and molybdenum compound to be added is not less than 0.2% by mass and not more than 1.0% by mass in relation to the mass of the cathode active material composed mainly of nickel hydroxide, having the coating layer of the cobalt compound.

[Claim 4] An alkaline storage battery according to claim 1, wherein the alkaline electrolytic solution contains sodium hydroxide.

[Name of the Document] Specification

[Title of Invention] Alkaline Storage Battery

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an alkaline storage battery such as a nickel-hydrogen battery, nickel-cadmium battery, etc., and in particular, to an alkaline storage battery comprising nickel cathodes (positive electrode) containing a cathode active material composed mainly of nickel hydroxide and an alkaline electrolytic solution.

[0002]

[Relevant Art]

The range of uses of secondary batteries (storage batteries) has lately become broader, and storage batteries have come to be used in a wide variety of equipment including personal computers, mobile phones, electric cars, hybrid cars, motor-operated bicycles, electric tools, etc., have been put to use as the power source of equipment requiring high output, such as electric cars, hybrid cars, motor-operated bicycles, electric tools, etc. In addition, the alkaline storage battery has become more significant because it can be used even in a high-temperature atmosphere.

[0003]

Accordingly, a demand has since arisen for an alkaline storage battery insusceptible to deterioration in recharge/discharge performance and recharge/discharge efficiency even if recharge/discharge operations are carried out in a high-temperature atmosphere. This is because, for example, when an alkaline storage battery is recharged at high temperature, recharge reaction and oxygen generation reaction compete with each other, so that the energy used to generate oxidation reaction (the recharge reaction) of nickel hydroxide as a cathode active material is also utilized for the oxygen generation reaction as well, thereby resulting in deterioration of recharge efficiency.

[0004]

Accordingly, in Patent Document of JP, H 8 - 222213, A, an alkaline storage battery has been proposed wherein a layer of an electrically conductive agent composed of a cobalt metal or cobalt compound is made to form on the

surface of cathode active material particles composed mainly of nickel hydroxide while one species of compound selected from the group consisting of a zirconium compound, niobium compound, molybdenum compound, and tungsten compound is introduced into cathodes comprising the cathode active material particles.

[0005]

If one species of compound selected from the group consisting of the zirconium compound, niobium compound, molybdenum compound, and tungsten compound is introduced into the cathodes as described above, the rate at which the cobalt compound coating the surface of the cathode active material composed mainly of nickel hydroxide is dissolved and precipitated in an alkaline electrolytic solution can decrease and the layer of the cobalt compound can become denser in structure, thereby enabling an excellent electrically conductive network to be maintained in the nickel cathode. Accordingly, the oxygen generating overvoltage becomes higher, so that the oxygen generation reaction can be inhibited, thereby enhancing recharging efficiency.

[0006]

[Problems to Be Resolved by the Invention]

However, the enhancement of the cycle life of the alkaline storage battery in high temperature, wherein one species of a compound selected from the group consisting of zirconium compound, niobium compound, molybdenum compound, and tungsten compound is introduced into the cathodes comprising the cathode active material provided with a layer of an electrically conductive agent composed of cobalt metal and a cobalt compound is far from satisfactory. This is presumably due to the fact that repeated recharge/discharge operations at high temperature will result in the dissolution of the zirconium compound etc. in the alkaline electrolytic solution, thereby causing damage to the cobalt compound (cobalt hydroxide) in the uppermost surface layer by reducing conductivity.

[0007]

That is, as a result of the initial recharge operation, the cobalt hydroxide in the uppermost surface layer is transformed into cobalt oxide with a higher degree of conductivity in order to be stabilized. Repeated recharge/discharge operations at high temperature causes the cobalt oxide to be reduced into cobalt hydroxide thereafter to be thereby dissolved and precipitated in an alkaline aqueous solution (an electrolytic solution). As a result, the conductivity of the

nickel cathodes is presumed to gradually deteriorate, leading to deterioration in cycle life.

[0008]

[0008]

The present invention has been developed in order to resolve the problem described as above by providing an alkaline storage battery with an excellent cycle life characteristic at high temperature, capable of preventing conductivity deterioration even if recharge/discharge operations repeatedly take place in a high temperature atmosphere.

[0009]

[Means of Solving the Problems]

To that end, the alkaline storage battery of the invention comprises nickel cathodes and an alkaline electrolytic solution, wherein at least one species of compound selected from the group consisting of a niobium compound, titanium compound, tungsten compound and molybdenum compound is introduced into the nickel cathodes comprising a cathode active material composed mainly of nickel hydroxide, which surface has a coating layer of a cobalt compound, whereas the alkaline electrolytic solution contains lithium hydroxide of not less than 0.6 mol / L and not more than 1.6 mol / L.

[0010]

If at least one species of a compound selected from the group consisting of niobium compound, titanium compound, tungsten compound, and molybdenum compound is introduced into the nickel cathodes as described above, the rate at which the cobalt compound coating the surface of an active material layer composed mainly of nickel hydroxide is dissolved and precipitated in the alkaline electrolytic solution can be decreased. Further, if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide, dissolution of the niobium compound, titanium compound, tungsten compound, and molybdenum compound therein can be inhibited.

[0011]

Thereby, the layer of the cobalt compound becomes denser in structure, and an excellent electrically conductive network is enabled to be maintained in the nickel cathodes. However, if the alkaline electrolytic solution contains 1.8 mol / L of lithium hydroxide, the lithium hydroxide is not easily dissolved so that

it is necessary to restrict the lithium hydroxide content of the alkaline electrolytic solution to not more than 1.6 mol / L.

[0012]

In this case, if the layer of the cobalt compound contains alkali metal ion, the conductivity of the layer of the cobalt compound is further enhanced, so that the layer of the cobalt compound is preferably a layer of a cobalt compound containing alkali metal ion. Further, it has been determined that the rate at which the cobalt compound coating the surface of the active material layer is dissolved and precipitated in the alkaline electrolytic solution is not effectively reduced if the amount of any compound, selected from the group consisting of niobium compound, titanium compound, tungsten compound, and molybdenum compound, added into the nickel cathodes together with the cathode active material, is less than 0.2% by mass in relation to the mass of the cathode active material.

[0013]

Further, if the amount of compound added is increased to more than 1.0% by mass in relation to the mass of the cathode active material, the amount of nickel hydroxide serving as an active material in the nickel cathodes is reduced, thereby decreasing discharge capacity. Accordingly, the amount of niobium compound, titanium compound, tungsten compound, or molybdenum compound to be added should preferably be within the range of 0.2 to 1.0% by mass in relation to the mass of the cathode active material.

[0014]

In case a niobium compound is used, it must preferably be made of a compound selected from the group consisting of Nb_2O_5 , Nb_2O_3 , NbO , NbO_2 , NaNbO_3 , LiNbO_3 , KNbO_3 , $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, and so forth. In case a titanium compound is used, it must preferably be made of a compound selected from the group consisting of TiO_2 , Ti_2O_3 , TiO , $\text{Na}_2\text{Ti}_3\text{O}_7$, Li_2TiO_3 , K_2TiO_3 and so forth. Further, in case a tungsten compound is used, it must preferably be made of a compound selected from the group consisting of WO_2 , WO_3 , Na_2WO_4 , Li_2WO_2 , K_2WO_4 and so forth. Further still, in case a molybdenum compound is used, it must preferably be made of a compound selected from the group consisting of MoO_3 , $\text{MoO}_3 \cdot \text{H}_2\text{O}$, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Li}_6\text{Mo}_7\text{O}_{24} \cdot 12\text{H}_2\text{O}$, K_2MoO_4 and so forth.

[0015]

[Embodiment of the Invention]

Embodiments of the invention are described in detail hereinafter. However, it is posited that the invention is not limited thereto, and various changes and modifications as appropriate may be made without departing from the spirit and scope of the invention.

1. Nickel Cathodes

(1) Fabrication of Cathode Active Material

While stirring an aqueous solution composed of a mixture of nickel sulfate, zinc sulfate, and cobalt sulfate, containing 3 parts by mass of zinc and 1 part by mass of cobalt against 100 parts by mass of nickel metal, respectively, an aqueous solution of sodium hydroxide was gradually added thereto and the pH of the reaction solution was maintained within the range of 13 and 14, thereby causing nickel hydroxide in grain form to be precipitated. An aqueous solution of cobalt sulfate was further added to the solution wherein the nickel hydroxide in grain form was precipitated, and the pH of the reaction solution being maintained at a range of 9 to 10, while spherical hydroxide particles composed mainly of nickel hydroxide were used as nuclei of crystals, thereby causing cobalt hydroxide to be precipitated around the respective nuclei.

[0016]

Thus, nickel hydroxide particles with a coating layer of cobalt hydroxide on the surface were obtained. Thereafter, alkaline heat treatment was applied to the nickel hydroxide particles, whereby an alkaline solution was sprayed thereto in a hot air flow. During the alkaline heat treatment, temperature was adjusted such that the temperature of the nickel hydroxide particles was kept at 60°C, and 35% by mass of an alkaline solution (aqueous solution of sodium hydroxide), equivalent to 5 times as much as the parts by mass of cobalt, were sprayed. Subsequently, temperature was raised until the temperature of the nickel hydroxide particles reached 90°C. Then, the nickel hydroxide particles were washed with water and dried at 60°C and thereafter turned into cathode active material. In so doing, nickel hydroxide powders (the cathode active material) with a highly conductive coating of a cobalt compound containing sodium (alkali metal ion), formed on the surface of the nickel hydroxide particles, were obtained.

[0017]

(2) Fabrication of Nickel Cathode

Subsequently, after making the mixture by adding Nb_2O_5 as a niobium compound to the cathode active material prepared in the above described manner, 200 g of a dispersion liquid containing 0.25% by mass of HPC (hydroxylpropyl cellulose) were added to and mixed with 500 g of the mixture, thereby producing an active material slurry. Thereafter, the active material slurry was filled in corresponding electrode base plates made of porous nickel 1.7 mm thick so as to reach a predetermined packing density. Subsequently, the respective electrode base plates were dried and rolled to a thickness of 0.75 mm, then cut to a predetermined size, thereby preparing non-sintered nickel cathodes a1, a2, a3, a4, a5, and a6, respectively.

[0018]

A non-sintered nickel cathode prepared by using active material slurry fabricated by adding Nb_2O_5 (niobium compound) so as to percentage of Nb_2O_5 in relation to the mass of the cathode active material when Nb_2O_5 was added be 0.1 % mass was designated as non-sintered nickel cathode a1. Similarly, a non-sintered nickel cathode prepared by using active material slurry fabricated by adding 0.3 % mass of Nb_2O_5 was designated as non-sintered nickel cathode a2, a nickel cathode prepared by using active material slurry fabricated by adding 0.5 % mass of Nb_2O_5 was designated as non-sintered nickel cathode a3, and a nickel cathode prepared by using active slurry fabricated by adding 0.7 % mass of Nb_2O_5 was designated as non-sintered nickel cathode a4, respectively.

[0019]

Furthermore, a non-sintered nickel cathode prepared by using active slurry fabricated by adding 1.0 % mass of Nb_2O_5 was designated as non-sintered nickel cathode a5, and a non-sintered nickel cathode prepared by using active slurry fabricated by adding 1.5 % mass of Nb_2O_5 was designated as non-sintered nickel cathode a6, respectively. And further, a non-sintered nickel cathode prepared by using active material slurry fabricated without adding Nb_2O_5 was designated as non-sintered nickel cathode x.

[0020]

2. Hydrogen Storing Alloy Anodes

(1) Fabrication of Anode Active Material

After mixing mesh metal (Mm), nickel (Ni: purity 99.9%), cobalt (Co), Manganese (Mn), and aluminum (Al) together at a predetermined mole ratio, respectively, the mixture obtained was subjected to induction heating in an argon atmosphere inside a high frequency induction furnace to be thereby turned into molten alloy. The molten alloy was thereafter poured into a mold by the publicly known method, and after cooling, an ingot of hydrogen storage alloy expressed by a composition formula $MmNi_aCo_bMn_cAl_d$ was prepared. The ingot of the hydrogen storage alloy was pulverized through a mechanical crushing method to about 60 μm in average grain size.

[0021]

(2) Fabrication of Hydrogen Storing Alloy Anode

Subsequently, hydrogen storage alloy paste was prepared by mixing 20 parts by mass of an aqueous solution of 5% by mass of polyethylene oxide (PEO) as a binder with 100 parts by mass of hydrogen storage alloy powders. The hydrogen storage alloy paste was thereafter applied to both surfaces of a core body made up of punching metal, and dried at room temperature. The workpiece thus obtained was cut to a predetermined size, thereby producing a hydrogen storage alloy anode.

[0022]

3. Preparation of Alkaline Electrolytic Solution

First, a two-component alkaline electrolytic solution prepared by mixing 5.5 mol / L of potassium hydroxide (KOH) with 0.5 mol / L of sodium hydroxide (NaOH), and the solution was designated as electrolytic solution e1. Further, a three-component alkaline solution was prepared by mixing 5.5 mol / L of potassium hydroxide (KOH), 0.5 mol / L of sodium hydroxide (NaOH), and 0.4 mol / L of lithium hydroxide (LiOH) together, and the solution was designated as electrolytic solution e2. Similarly, an electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 0.6 mol / L of LiOH together was designated as electrolytic solution e3, and a electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 0.8 mol / L of LiOH together was designated as electrolytic solution e4.

[0023]

And further, an electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.0 mol / L of LiOH together was designated as

electrolytic solution e5, and an electrolytic solution prepared by by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.2 mol / L of LiOH together was designated as electrolytic solution e6. Further, an electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.4 mol / L of LiOH together was designated as electrolytic solution e7, and an electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.6 mol / L of LiOH together was designated as electrolytic solution e8. Further, an electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.8 mol / L of LiOH together was designated as electrolytic solution e9, and an electrolytic solution prepared by mixing 6.6 mol / L of KOH with 0.6 mol / L of NaOH was designated as electrolytic solution e10.

[0024]

4. Nickel-Hydrogen Storage Batteries

Now, the non-sintered nickel cathode a3 (with the addition of 0.5% by mass of Nb_2O_5) and the non-sintered nickel cathode x (without addition of Nb_2O_5), respectively prepared in the above described manner, together with the hydrogen storage alloy anode, with a separator made of polypropylene-nonwoven fabric, interposed therebetween, were wound about in a spiral form, thereby creating a electrode group for respective batteries to be fabricated. Subsequently, after inserting the electrode groups into corresponding outer cases, respectively, an anode lead extending from an anode of the respective electrode groups was connected to each outer case while a cathode lead extending from a cathode was connected to each cathode lid provided on a sealing body. Thereafter, the electrolytic solutions e1 through e10, prepared in the above described manner, were poured into each outer case, respectively, and the opening of each outer case was sealed with each sealing body, thereby fabricating nickel-hydrogen batteries with nominal capacity 1000 mAh, A1 through A10 and Y, respectively, as follows.

[0025]

A battery prepared by using the nickel cathode a3 and the electrolytic solution e1 was designated as battery A1, a battery prepared by using the nickel cathode a3 and the electrolytic solution e2 was designated as battery A2, a battery prepared by using the nickel cathode a3 and the electrolytic solution e3 was designated as battery A3, a battery prepared by using the nickel cathode a3 and the electrolytic solution e4 was designated as battery A4, a battery prepared

by using the nickel cathode a3 and the electrolytic solution e5 was designated as battery A5, a battery prepared by using the nickel cathode a3 and the electrolytic solution e6 was designated as battery A6, a battery prepared by using the nickel cathode a3 and the electrolytic solution e7 was designated as battery A7, a battery prepared by using the nickel cathode a3 and the electrolytic solution e8 was designated as battery A8, a battery prepared by using the nickel cathode a3 and the electrolytic solution e9 was designated as battery A9, and a battery prepared by using the nickel cathode a3 and the electrolytic solution e10 was designated as battery A10, respectively. Further, the battery prepared by using the nickel cathode x and the electrolytic solution e1 was designated as the battery Y.

[0026]

5. Test

(1) Measurement of Initial Discharge Capacity

The respective batteries A1 through A10 and Y, fabricated in the manner described above, the respective batteries were recharged with recharge current at 100 mA (0.1ItmA) at a temperature of 25°C for 16 hours, and subsequently discharged with discharge current at 1000 mA (1ItmA) until each battery reached a voltage of 1.0V and acquired an initial discharge capacity (mAh) from discharge time. The test results obtained are shown in Table 1 below.

[0027]

(2) Measurement of High-Temperature Cyclic Characteristic (Capacity Maintaining Ratio)

Further, the respective batteries A1 through A10 and Y fabricated in the manner described above were recharged with recharge current at 100 mA (0.1ItmA) at a temperature of 60°C for 16 hours, and subsequently discharged with discharge current at 500 mA (0.5ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle. Thereafter, recharge/discharge cycle tests were repeatedly conducted until the discharge capacity of each battery at 60°C was reduced to not more than 80% of its discharge capacity determined at the end of the first cycle, which was defined as capacity maintaining ratio (cycle). The test results obtained are shown in Table 1 below.

[0028]

[Table 1]

battery type	nickel Cathode		electrolytic solution composition (mol / L)		initial discharge capacity (mAh)	capacity maintaining ratio (cycle)
	Type	Nb ₂ O ₅	type	KOH:NaOH:LiOH		
A1	a3	0.5	e1	5.5 : 0.5 : 0.0	870	290
A2	a3	0.5	e2	5.5 : 0.5 : 0.4	867	300
A3	a3	0.5	e3	5.5 : 0.5 : 0.6	866	380
A4	a3	0.5	e4	5.5 : 0.5 : 0.8	864	385
A5	a3	0.5	e5	5.5 : 0.5 : 1.0	866	385
A6	a3	0.5	e6	5.5 : 0.5 : 1.2	860	445
A7	a3	0.5	e7	5.5 : 0.5 : 1.4	861	450
A8	a3	0.5	e8	5.5 : 0.5 : 1.6	860	445
A9	a3	0.5	e9	5.5 : 0.5 : 1.8	860	440
A10	a3	0.5	e10	6.6 : 0.6 : 0.0	866	305
Y	a3	0.0	e1	5.5 : 0.5 : 0.0	875	100

[0029]

As is evident from Table 1 above, the batteries A1 through A10 using the nickel cathode a3 with addition of 0.5% by mass of Nb₂O₅ (niobium compound), have a higher capacity maintaining ratio (high-temperature cycle characteristic) compared to that of the battery Y using the nickel cathode Ax without addition of Nb₂O₅, which has a capacity maintaining ratio of as low as 100.

This is because if recharge/discharge operations are carried out in a high-temperature atmosphere without addition of Nb₂O₅, cobalt oxyhydroxide (CoOOH) resulting from oxidation of cobalt metal and cobalt compound is reduced to cobalt hydroxide {Co(OH)₂} to be thereby dissolved into an alkaline electrolytic solution, so the electrically conductive network is susceptible to breakdown, resulting in deterioration of the capacity maintaining ratio.

On the other hand, if Nb₂O₅ is added, reduction of a cobalt oxide containing sodium to cobalt hydroxide to be thereby dissolved in an alkaline electrolytic solution is inhibited at the time of discharge even if recharge/discharge operations are carried out in a high-temperature atmosphere, so that the electrically conductive network is deemed maintained, resulting in enhancement of the capacity maintaining ratio.

[0030]

Further, even if Nb₂O₅ were added but the alkaline electrolytic solution does not contain lithium hydroxide (the batteries A1, A10), the capacity maintaining ratio would be 290 and 305, respectively, and if the lithium

hydroxide content is low (the battery A2), the capacity maintaining ratio would be 300. Meanwhile, the capacity maintaining ratio is enhanced if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide (the batteries A1 through A9). In this connection, by plotting such a relationship on a graph where lithium hydroxide content (mol / L) in the alkaline electrolytic solution is plotted on the horizontal axis and the capacity maintaining ratio (cycle) is plotted on the vertical axis, a curve denoted by the sign C (symbol \diamond) in Fig. 1 is obtained.

[0031]

As can be seen in Fig. 1, the amount of lithium hydroxide that the alkaline electrolytic solution should preferably be not less than 0.6 mol / L and not more than 1.6 mol / L, or preferably within the range of 1.2 to 1.6 mol / L. This is because if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide, dissolution of the niobium compound therein would be inhibited and if the solution contains not less than 1.2 mol / L of lithium hydroxide dissolution of the niobium compound in the alkaline electrolytic solution would be inhibited further. In the case of battery A9 involving 1.8 mol / L of lithium hydroxide, however, the lithium hydroxide is not easily dissolved in the alkaline electrolytic solution although the capacity maintaining ratio was found to be high, so that lithium hydroxide content should be limited to not more than 1.6 mol / L.

[0032]

Furthermore, as in the case of lithium hydroxide, sodium hydroxide has the effect of inhibiting dissolution of Nb_2O_5 (niobium compound) in the alkaline electrolytic solution. However, it is presumed that if sodium hydroxide content is increased, a compound would form from the niobium compound and sodium hydroxide on the surface of a nickel cathode and cause the liquid containing ratio of the nickel cathode to increase, thereby causing the nickel cathode to puff up. Because puffing up of the nickel cathode would lead to an increase in internal resistance of the battery, it is preferable not to increase the sodium hydroxide content.

[0033]

6. Effect of Increasing the Amount of Niobium Compound (Nb_2O_5) Added

Thereafter, the effect of increasing the amount of Nb_2O_5 (niobium

compound) was studied. Now, using the non-sintered nickel cathodes a1 through a6, x and the hydrogen storage alloy anode, prepared in the above described manner, respectively, together with the electrolytic solution e7 (the electrolytic solution prepared by mixing 5.5 mol / L of KOH, 0.5 mol / L of NaOH, and 1.4 mol / L of LiOH together), nickel-hydrogen batteries with nominal capacity of 1000 mAh, A11 through A16 and X, respectively, are fabricated in the same way as previously described.

[0034]

A battery prepared by using the non-sintered nickel cathode a1 was designated as battery A11, a battery prepared by using the non-sintered nickel cathode a2 was designated as battery A12, a battery prepared by using the non-sintered nickel cathode a3 was designated as battery A13, a battery prepared by using the non-sintered nickel cathode a4 was designated as battery A14, a battery prepared by using the non-sintered nickel cathode a5 was designated as battery A15, and a battery prepared by using the non-sintered nickel cathode a6 was designated as battery A16, respectively. Further, a battery prepared by using the non-sintered nickel cathode x was designated as battery X.

[0035]

The respective batteries A11 through A16 and X, fabricated in the manner described above, were recharged with recharge current at 100 mA (0.1ItmA) at 25°C for 16 hours, and subsequently discharged with discharge current at 1000 mA (1ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle and thereafter, recharge/discharge cycle tests were repeatedly conducted. The test results obtained are shown in Table 2 below. Further, the respective batteries A11 through A16 and X, were recharged with recharge current at 100mA (0.1ItmA) at 60°C for 16 hours, and subsequently discharged with discharge current at 500mA (0.5ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle and thereafter, recharge/discharge cycle tests were repeatedly conducted until the discharge capacity of each battery at 60°C was reduced to not more than 80% of its discharge capacity determined at the end of the first cycle, which was defined as the capacity maintaining ratio (cycle). The test results obtained are shown in Table 2 below.

[0036]

[Table 2]

battery type	nickel Cathode		electrolytic solution composition (mol / L)		Initial discharge capacity (mAh)	capacity maintaining ratio (cycle)
	Type	Nb ₂ O ₅	type	KOH:NaOH: LiOH		
A11	a1	0.1	e7	5.5 : 0.5 : 1.4	874	250
A12	a2	0.2	e7	5.5 : 0.5 : 1.4	872	440
A13	a3	0.5	e7	5.5 : 0.5 : 1.4	866	450
A14	a4	0.7	e7	5.5 : 0.5 : 1.4	862	440
A15	a5	1.0	e7	5.5 : 0.5 : 1.4	860	445
A16	a6	1.5	e7	5.5 : 0.5 : 1.4	824	430
X	x	0.0	e7	5.5 : 0.5 : 1.4	874	110

[0037]

As is evident from Table 2 shown below, as in the case of the battery X without the addition of Nb₂O₅ (niobium compound), the capacity maintaining ratio (high-temperature cycle characteristic) is low. Further as in the case of the battery A11, if the amount of Nb₂O₅ added is as little as 0.1% by mass in relation to the mass of the cathode active material, there is no improvement in the capacity maintaining ratio (high-temperature cycle characteristic). Further, still, as in the case of the battery A16, if the amount of Nb₂O₅ added is increased to 1.5% by mass in relation to the mass of the cathode active material, the initial discharge capacity will decrease. It may thus be concluded that the amount of Nb₂O₅ (niobium compound) to be added should preferably be within the range of 0.2 to 1.0% by mass in relation to the mass of the cathode active material (composed mainly of nickel hydroxide coated with a cobalt compound). In this connection, the niobium compound to be added to the cathode active material may be made of a compound selected from the group consisting of Nb₂O₃, NbO, NbO₂, NaNbO₃, LiNbO₃, KNbO₃, Nb₂O₅·xH₂O, and so forth, besides Nb₂O₅.

[0038]

7. Studies on Compounds Added

Studies have also been made of cases involving the addition of a titanium compound (for example, TiO₂), tungsten compound (for example, WO₂), and molybdenum compound (for example, MoO₃) to the cathode active material.

[0039]

(1) Titanium Compound

After preparing an active material slurry by adding TiO₂ as a titanium compound to the cathode active material (composed mainly of nickel hydroxide

coated with a cobalt compound) such that the amount of TiO_2 to be added corresponds to 0.5% by mass in relation to the mass of the cathode active material, the active material slurry was poured into an electrode base plate made of porous nickel as previously described. Subsequently, the electrode base plate was dried and rolled then cut to a predetermined size, thereby preparing a nickel cathode b.

[0040]

Thereafter, the non-sintered nickel cathode b, and the hydrogen storage alloy anode prepared as previously described, with a separator made of polypropylene-nonwoven fabric, interposed therebetween, were wound about in a spiral form, thereby creating electrode groups for respective batteries to be fabricated. Subsequently, after inserting each electrode group into corresponding outer cases, an anode lead extending from an anode of each respective electrode group was connected to each outer case while a cathode lead extending from a cathode was connected with a cathode lid provided on a sealing body. Thereafter, the electrolytic solutions e1 through e10, prepared as previously described, were poured into the outer cases, respectively, and the opening of each outer case was sealed with the sealing body, thereby fabricating nickel-hydrogen storage batteries with a nominal capacity of 1000 mAh, B1 through B10, respectively.

[0041]

A Battery prepared by using the electrolytic solution e1 was designated as battery B1, a battery prepared by using the electrolytic solution e2 was designated as battery B2, a battery prepared by using the electrolytic solution e3 was designated as battery B3, a battery prepared by using the electrolytic solution e4 was designated as battery B4, a battery prepared by using the electrolytic solution e5 was designated as battery B5, a battery prepared by using the electrolytic solution e6 was designated as battery B6, respectively. Further, a battery prepared by using the electrolytic solution e7 was designated as battery B7, a battery prepared by using the electrolytic solution e8 was designated as battery B8, a battery prepared by using the electrolytic solution e9 was designated as battery B9, and a battery prepared by using the electrolytic solution e10 was designated as the battery B10, respectively.

[0042]

Thereafter, the respective batteries B1 through B10, fabricated in the manner described above, were recharged with recharge current at 100 mA (0.1ItmA) at 25°C for 16 hours, and subsequently discharged with discharge current at 1000 mA (1ItmA) until each battery reached a voltage of 1.0V and acquired an initial discharge capacity from discharge time. The test results obtained are shown in Table 3 below. Further, the respective batteries B through B10, were recharged with recharge current at 100 mA (0.1ItmA) at 60°C for 16 hours, and subsequently discharged with discharge current at 500 mA (0.5ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle. Thereafter, recharge/discharge cycle tests were repeatedly conducted until the discharge capacity of each battery at 60°C was reduced to not more than 80% of its discharge capacity determined at the end of the first cycle, which was defined as capacity maintaining ratio (cycle). The test results obtained as well as the results concerning the batteries X and Y are shown in Table 3 below.

[0043]

[Table 3]

battery type	nickel cathode		electrolytic solution composition (mol / L)		Initial discharge capacity (mAh)	capacity maintaining ratio (cycle)
	type	TiO ₂	type	KOH:NaOH: LiOH		
B1	b	0.5	e1	5.5 : 0.5 : 0.0	868	250
B2	b	0.5	e2	5.5 : 0.5 : 0.4	866	265
B3	b	0.5	e3	5.5 : 0.5 : 0.6	864	355
B4	b	0.5	e4	5.5 : 0.5 : 0.8	863	360
B5	b	0.5	e5	5.5 : 0.5 : 1.0	865	370
B6	b	0.5	e6	5.5 : 0.5 : 1.2	861	425
B7	b	0.5	e7	5.5 : 0.5 : 1.4	860	430
B8	b	0.5	e8	5.5 : 0.5 : 1.6	861	425
B9	b	0.5	e9	5.5 : 0.5 : 1.8	859	430
B10	b	0.5	e10	6.6 : 0.6 : 0.0	865	260
X	x	0.0	e7	5.5 : 0.5 : 1.4	874	110
Y	x	0.0	e1	5.5 : 0.5 : 0.0	875	100

[0044]

As is evident from Table 3 above, the batteries B1 through B10 using the nickel cathode b with addition of 0.5% by mass of TiO₂ (titanium compound), have a higher capacity maintaining ratio (high-temperature cycle characteristic) compared with that of the case of the batteries Y using the nickel cathode x without addition of TiO₂, whose capacity maintaining ratio is low or within the range of 100.

This is because if recharge/discharge operations are carried out in a high-temperature atmosphere without addition of TiO_2 , cobalt oxyhydroxide (CoOOH) resulting from oxidation of cobalt metal and cobalt compound is reduced to cobalt hydroxide $\{\text{Co}(\text{OH})_2\}$ to be thereby dissolved into an alkaline electrolytic solution, the electrically conductive network is susceptible to breakdown, resulting in deterioration of the capacity maintaining ratio.

On the other hand, if TiO_2 is added, reduction of a cobalt oxide containing sodium to cobalt hydroxide to be thereby dissolved in an alkaline electrolytic solution is inhibited at the time of discharge even if recharge/discharge operations are carried out in a high temperature atmosphere, so that the electrically conductive network is deemed maintained, resulting in enhancement of the capacity maintaining ratio.

[0045]

Further, even if TiO_2 were added but if alkaline electrolytic solution does not contain lithium hydroxide (the batteries B1, B10), the capacity maintaining ratio would be 250 cycles and 260 cycles, respectively, while if the lithium hydroxide content is low (the battery B2), the capacity maintaining ratio would be 265 cycles. Meanwhile, the capacity maintaining ratio is enhanced if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide (the batteries B1 through B9). In this connection, by plotting such a relationship on a graph where lithium hydroxide content (mol / L) in the alkaline electrolytic solution is plotted on the horizontal axis and the capacity maintaining ratio (cycle) is plotted on the vertical axis, a curve denoted by the sign F (symbol \square) is obtained as shown in Fig. 1.

[0046]

As is evident in Fig. 1, the preferable amount of lithium hydroxide in the alkaline electrolytic solution should be not less than 0.6 mol / L and not more than 1.6 mol / L, or preferably within the range of 1.2 to 1.6 mol / L. This is because if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide, dissolution of TiO_2 in the alkaline electrolytic solution would be inhibited, and if the solution contains not less than 1.2 mol / L of lithium hydroxide, dissolution of TiO_2 in the alkaline electrolytic solution would be inhibited further. In the case of the battery A9 which contains 1.8 mol / L of lithium hydroxide, the lithium hydroxide is not easily dissolved in the alkaline

electrolytic solution although the capacity maintaining ratio was found to be high, so that lithium hydroxide content should be limited to not more than 1.6 mol / L.

[0047]

Furthermore, as in the case of lithium hydroxide, sodium hydroxide has the effect of inhibiting dissolution of TiO_2 (titanium compound) in the alkaline electrolytic solution. However, it is presumed that if sodium hydroxide content is increased, a compound would form from TiO_2 and sodium hydroxide on the surface of a nickel cathode and cause the liquid containing ratio of the nickel cathode to increase, thereby causing the nickel cathode to puff up. Because puffing up of the nickel cathode would effectively increase in internal resistance of the battery, it is preferable not to increase the sodium hydroxide content. Further, the amount of TiO_2 to be added should preferably be within the range of 0.2 to 1.0% by mass as in the case of the niobium compound as previously described. In this connection, the titanium compound to be added to the cathode active material may be made of any compound selected from the group consisting of Ti_2O_3 , TiO , $\text{Na}_2\text{Ti}_3\text{O}_7$, Li_2TiO_3 , K_2TiO_3 and so forth, besides TiO_2 .

[0048]

(2) Tungsten Compounds

After preparing an active material slurry by adding WO_2 as a tungsten compound to the cathode active material (composed mainly of nickel hydroxide coated with a cobalt compound) such that the amount of WO_2 to be added corresponds to 0.5% by mass in relation to the mass of the cathode active material, the active material slurry was poured into an electrode base plate made of porous nickel as previously described. Subsequently, the electrode base plate was dried and rolled, then cut to a predetermined size, thereby preparing a nickel cathode c.

[0049]

Thereafter, the nickel cathode c and the hydrogen storage alloy anode prepared as previously described, with a separator made of polypropylene-nonwoven fabric, interposed therebetween, were wound about in a spiral form, thereby producing electrode groups for respective batteries to be fabricated. Subsequently, after inserting each respective electrode group into corresponding outer cases, an anode lead extending from an anode of the respective electrode group was connected to each outer case while a cathode lead

extending from a cathode was connected to a cathode lid provided on a sealing body. Thereafter, the electrolytic solutions e1 through e10, prepared as previously described, were poured into the outer case, respectively, and the opening of each outer case was sealed with the sealing body, thereby fabricating nickel-hydrogen batteries with a nominal capacity of 1000 mAh, C1 through C10, respectively designated.

[0050]

A battery prepared by using the electrolytic solution e1 was designated as battery C1, a battery prepared by using the electrolytic solution e2 was designated as battery C2, a battery prepared by using the electrolytic solution e3 was designated as battery C3, a battery prepared by using the electrolytic solution e4 was designated as battery C4, a battery prepared by using the electrolytic solution e5 was designated as battery C5, a battery prepared by using the electrolytic solution e6 was designated as battery C6, respectively. Further, a battery prepared by using the electrolytic solution e7 was designated as battery C7, a battery prepared by using the electrolytic solution e8 was designated as battery C8, a battery prepared by using the electrolytic solution e9 was designated as battery C9, and a battery prepared by using the electrolytic solution e10 was designated as battery C10, respectively.

[0051]

Thereafter, the respective batteries C1 through C10, fabricated in the manner described above, were recharged with recharge current at 100 mA (0.1ItmA) at 25°C for 16 hours, and subsequently discharged with discharge current at 1000 mA (1ItmA) until each battery reached a voltage of 1.0V and acquired an initial discharge capacity from discharge time. The test results obtained are shown in Table 4 below. Further, the respective batteries C1 through C10 were recharged with recharge current at 100mA (0.1ItmA) at 60°C for 16 hours, and subsequently discharged with discharge current at 500mA (0.5ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle. Thereafter, recharge/discharge cycle tests were repeatedly conducted until the discharge capacity of each battery at 60°C diminished by not more than 80% of its discharge capacity determined at the end of the first cycle, which was defined as the capacity maintaining ratio (cycle). The test results obtained as well as the results concerning the batteries Cx1 and Cx2, respectively,

are shown in Table 4 below.

[0052]

[Table 4]

battery type	nickel cathode		electrolytic solution composition (mol / L)		initial discharge capacity (mAh)	capacity maintaining ratio (cycle)
	type	WO ₂	type	KOH:NaOH: LiOH		
C1	c	0.5	e1	5.5 : 0.5 : 0.0	869	270
C2	c	0.5	e2	5.5 : 0.5 : 0.4	865	285
C3	c	0.5	e3	5.5 : 0.5 : 0.6	863	360
C4	c	0.5	e4	5.5 : 0.5 : 0.8	863	380
C5	c	0.5	e5	5.5 : 0.5 : 1.0	862	390
C6	c	0.5	e6	5.5 : 0.5 : 1.2	861	430
C7	c	0.5	e7	5.5 : 0.5 : 1.4	860	435
C8	c	0.5	e8	5.5 : 0.5 : 1.6	862	435
C9	c	0.5	e9	5.5 : 0.5 : 1.8	858	435
C10	c	0.5	e10	6.6 : 0.6 : 0.0	864	275
X	x	0.0	e7	5.5 : 0.5 : 1.4	874	110
Y	x	0.0	e1	5.5 : 0.5 : 0.0	875	100

[0053]

As is evident from Table 4 above, the batteries C1 through C10 using the nickel cathode c with the addition of 0.5% by mass of WO₂ (tungsten compound) have a higher capacity maintaining ratio (high-temperature cycle characteristic) compared to that of the batteries Y using the nickel cathode x without addition of WO₂, whose a capacity maintaining ratio is low or within the range of 100.

This is because if recharge/discharge operations are carried out in a high-temperature atmosphere without addition of WO₂, cobalt oxyhydroxide (CoOOH), resulting from oxidation of cobalt metal and cobalt compound, is reduced to cobalt hydroxide {Co(OH)₂} to be thereby dissolved in an alkaline electrolytic solution, so that the electrically conductive network is susceptible to breakdown, resulting in deterioration of the capacity maintaining ratio.

On the other hand, if WO₂ is added, reduction of a cobalt oxide containing sodium to cobalt hydroxide to be thereby dissolved into an alkaline electrolytic solution is inhibited at the time of discharge even if recharge/discharge operations are carried out in a high temperature atmosphere, so that the electrically conductive network is deemed maintained, resulting in enhancement of the capacity maintaining ratio.

[0054]

Further, even if WO₂ were added, but the alkaline electrolytic solution does not contain lithium hydroxide (the batteries C1, C10), the capacity

maintaining ratio would be 270 cycles and 275 cycles, respectively, and if the lithium hydroxide content is low (the battery C2), the capacity maintaining ratio would be 285 cycles. Meanwhile, the capacity maintaining ratio is enhanced if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide (the batteries C2 through C9). In this connection, by plotting such a relationship on a graph where lithium hydroxide content (mol / L) of the alkaline electrolytic solution is plotted on the horizontal axis and the capacity maintaining ratio (cycle) is plotted on the vertical axis, a curve denoted by sign C (symbol Δ) is obtained as shown in Fig. 1.

[0055]

Based on the results shown in Fig. 1, the preferable amount lithium hydroxide that the alkaline electrolytic solution should contain is not less than 0.6 mol / L and not more than 1.6 mol / L, or preferably within the range of 1.2 to 1.6 mol / L. This is because if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide dissolution of WO_2 in the alkaline electrolytic solution would be inhibited, and if the solution contains not less than 1.2 mol / L of lithium hydroxide, dissolution of WO_2 in the alkaline electrolytic solution would be inhibited further. In the case of the battery C9 involving 1.8 mol / L of lithium hydroxide, however, the lithium hydroxide is not easily dissolved in the alkaline electrolytic solution although the capacity maintaining ratio was found to be high, so that lithium hydroxide content should be limited to not more than 1.6 mol / L.

[0056]

Furthermore, as in the case of lithium hydroxide, sodium hydroxide has the effect of inhibiting dissolution of WO_2 (tungsten compound) in the alkaline electrolytic solution. However, it is presumed that if sodium hydroxide content is increased, a compound would form from WO_2 and sodium hydroxide on the surface of a nickel cathode and cause the liquid containing ratio of the nickel cathode to increase, thereby causing the nickel cathode to puff up. Because puffing up of the nickel cathode would effectively increase in internal resistance of the battery, it is preferable not to increase the sodium hydroxide content. Further, the amount of WO_2 (tungsten compound) to be added should preferably be within the range of 0.2 to 1.0% by mass as in the case of Nb_2O_5 (niobium compound) as previously described. In this connection, the tungsten compound

to be added to the cathode active material may be made of any compound selected from the group consisting of WO_3 , Na_2WO_4 , Li_2WO_2 , K_2WO_4 and so forth, besides WO_2 .

[0057]

(3) Molybdenum Compounds

After preparing an active material slurry by adding MoO_3 as a molybdenum compound to the cathode active material (composed mainly of nickel hydroxide coated with a cobalt compound) prepared as previously described such that the amount of MoO_3 to be added corresponds to 0.5% by mass in relation to the mass of the cathode active material, the active material slurry was poured into an electrode base plate made of porous nickel as previously described. Subsequently, the electrode base plate was dried and rolled then cut to a predetermined size, thereby preparing a non-sintered nickel cathode d.

[0058]

Thereafter, the non-sintered nickel cathode d and the hydrogen storage alloy anode prepared as previously described, with a separator made of polypropylene-nonwoven fabric, interposed therebetween, were wound about in a spiral form, thereby forming electrode groups, respectively. Subsequently, after inserting the respective electrode groups into respective outer cases, an anode lead extending from an anode of each respective electrode group was connected to each outer case while a cathode lead extending from a cathode was connected to a cathode lid provided on a sealing body. Thereafter, the electrolytic solutions e1 through e10, prepared as previously described, were poured into the outer cases, respectively, and the opening of each outer case was sealed with the sealing body, thereby fabricating nickel-hydrogen batteries with nominal capacity of 1000 mAh, D1 through D10, respectively.

[0059]

A batter prepared by using the electrolytic solution e1 was designated as battery D1, a battery prepared by using the electrolytic solution e2 was designated as battery D2, a battery prepared by using the electrolytic solution e3 was designated as battery D3, a battery prepared by using the electrolytic solution e4 was designated as battery D4, a battery prepared by using the electrolytic solution e5 was designated as battery D5, and a battery prepared by using the electrolytic solution e6 was designated as battery D6, respectively.

Furthermore, a battery prepared by using the electrolytic solution e7 was designated as battery D7, a battery prepared by using the electrolytic solution e8 was designated as battery D8, a battery prepared by using the electrolytic solution e9 was designated as D9, and a battery prepared by using the electrolytic solution e10 was designated as battery D10, respectively.

[0060]

Thereafter, the respective batteries D1 through D10 fabricated in the manner described above were recharged with recharge current at 100 mA (0.1ItmA) at 25°C for 16 hours, and subsequently discharged with discharge current at 1000 mA (1ItmA) until each battery reached a voltage of 1.0V and acquired an initial discharge capacity from discharge time. The test results obtained are shown in Table 5 below. Further, the batteries D1 through D10 fabricated in the manner described above were recharged with recharge current at 100 mA (0.1ItmA) at 60°C for 16 hours, and subsequently discharged with discharge current at 500 mA (0.5ItmA) until each battery reached a voltage of 1.0V, which was defined as one cycle. Thereafter, recharge/discharge cycle tests were repeatedly conducted until the discharge capacity of each battery at 60°C was reduced to not more than 80% of its discharge capacity determined at the end of the first cycle, which was defined as capacity maintaining ratio (cycle). The test results obtained as well as the results concerning the batteries X and Y are shown in Table 5 below.

[0061]

[Table 5]

battery type	nickel cathode		electrolytic solution composition (mol / L)		initial discharge capacity (mAh)	capacity maintaining ratio (cycle)
	Type	MoO ₃	type	KOH: NaOH: LiOH		
D1	d	0.5	e1	5.5 : 0.5 : 0.0	871	255
D2	d	0.5	e2	5.5 : 0.5 : 0.4	868	260
D3	d	0.5	e3	5.5 : 0.5 : 0.6	866	350
D4	d	0.5	e4	5.5 : 0.5 : 0.8	862	365
D5	d	0.5	e5	5.5 : 0.5 : 1.0	864	375
D6	d	0.5	e6	5.5 : 0.5 : 1.2	861	420
D7	d	0.5	e7	5.5 : 0.5 : 1.4	860	425
D8	d	0.5	e8	5.5 : 0.5 : 1.6	862	430
D9	d	0.5	e9	5.5 : 0.5 : 1.8	857	435
D10	d	0.5	e10	6.6 : 0.6 : 0.0	865	260
X	x	0.0	e7	5.5 : 0.5 : 1.4	874	110
Y	x	0.0	e1	5.5 : 0.5 : 0.0	875	100

[0062]

As is evident from Table 5 above, the batteries D1 through D10 using the nickel cathode d with the addition of 0.5% by mass of MoO_3 (molybdenum compound) have a higher capacity maintaining ratio (high-temperature cycle characteristic) compared to that of the battery Y using the nickel cathode x without addition of MoO_3 , respectively, whose capacity maintaining ratio is low or within the range of 110 to 100 cycles.

This is because upon recharge/discharge in a high-temperature atmosphere without addition of MoO_3 , cobalt oxyhydroxide (CoOOH), resulting from oxidation of cobalt metal and cobalt compound is reduced to cobalt hydroxide $\{\text{Co}(\text{OH})_2\}$ to be thereby dissolved in an alkaline electrolytic solution, so that the electrically conductive network is susceptible to breakdown, resulting in deterioration of the capacity maintaining ratio.

On the other hand, if MoO_3 is added, reduction of a cobalt oxide containing sodium to cobalt hydroxide to be thereby dissolved into an alkaline electrolytic solution is inhibited at the time of discharge even if recharge/discharge operations are carried out in a high temperature atmosphere, so that the electrically conductive network is deemed maintained, resulting in enhancement of the capacity maintaining ratio.

[0063]

Further, it was determined that even if MoO_3 were added but the alkaline electrolytic solution does not contain lithium hydroxide, the capacity maintaining ratio is low (the batteries D1, D10), would be 255 cycles, and 260 cycles, respectively, while if the lithium hydroxide content is low (the battery D2), the capacity maintaining ratio would be 260 cycles. Meanwhile, the capacity maintaining ratio is enhanced if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide (the batteries D2 through D9). In this connection, by plotting such a relationship on a graph where lithium hydroxide content (mol / L) of the alkaline electrolytic solution is plotted on the horizontal axis and the capacity maintaining ratio (cycle) is plotted on the vertical axis, a curve denoted by sign H (symbol O) is obtained as shown in Fig. 1.

[0064]

Based on the results shown in Fig. 1, the preferable amount of lithium hydroxide that the alkaline electrolytic solution should contain is not less than

0.6 mol / L and not more than 1.6 mol / L, or preferably within the range of 1.2 to 1.6 mol / L. This is because if the alkaline electrolytic solution contains not less than 0.6 mol / L of lithium hydroxide dissolution of MoO_3 therein would be inhibited, and if the solution contains not less than 1.2 mol / L of lithium hydroxide dissolution of MoO_3 therein would be inhibited further. In the case of the battery A9 involving 1.8 mol / L of lithium hydroxide, however, lithium hydroxide is not easily dissolved in the alkaline electrolytic solution although the capacity maintaining ratio is high, so that lithium hydroxide content should be limited to not more than 1.6 mol / L.

[0065]

Furthermore, as in the case of lithium hydroxide, sodium hydroxide has the effect of inhibiting dissolution of MoO_3 (molybdenum compound) in the alkaline electrolytic solution. However, it is presumed that if sodium hydroxide content is increased, a compound would form from MoO_3 and sodium hydroxide on the surface of the nickel cathode and cause the liquid containing ratio of the nickel cathode to increase, thereby causing the nickel cathode to puff up. Because puffing up of the nickel cathode would lead to an increase in internal resistance of the battery, it is preferable not to increase the sodium hydroxide content. Further, the amount of MoO_3 (molybdenum compound) to be added should preferably be within the range of 0.2 to 1.0% by mass as in the case of niobium compound (Nb_2O_5) previously described. In this case, the molybdenum compound to be added to the cathode active material may be made of a compound selected from the group consisting of $\text{MoO}_3 \cdot \text{H}_2\text{O}$, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Li}_6\text{Mo}_7\text{O}_{24} \cdot 12\text{H}_2\text{O}$, K_2MoO_4 and so forth, besides MoO_3 .

[0066]

[Advantageous Effect of the Invention]

As described hereinbefore, under the invention, at least one species of a compound selected from the group consisting of niobium compound, titanium compound, tungsten compound, and molybdenum compound is introduced into the nickel cathodes provided with the cathode active material composed mainly of nickel hydroxide which surface has a coating layer of cobalt compound. Accordingly, the rate at which the cobalt compound coating the surface of the active material layer composed mainly of the nickel hydroxide is dissolved and precipitated in the alkaline electrolytic solution can decrease and the layer of the

cobalt compound can become to turn denser in structure, thereby enabling the electrically conductive network to be improved. Further, since not less than 0.6 mol / L of lithium hydroxide is contained in the alkaline electrolytic solution; it becomes possible to inhibit dissolution of the niobium compound, titanium compound, tungsten compound, or molybdenum compound in the alkaline electrolytic solution. This will enable an excellent electrically conductive network to be maintained.

[Brief Description of the Drawings]

[Fig. 1] A graph showing the relationship between lithium hydroxide content in an alkaline electrolytic solution (mol / L), and the capacity maintaining ratio (cycle).

[Name of the Document] Abstract

[The Problem to be Solved]

The present invention has been developed in order to resolve the problem described as above by providing an alkaline storage battery with an excellent cycle life characteristic at high temperature, capable of preventing conductivity deterioration even if recharge/discharge operations repeatedly take place in a high temperature atmosphere.

[The Means of Solving the Problem]

With an alkaline storage battery according to the invention, a coating layer of a cobalt compound is provided on the surface a cathode active material composed mainly of nickel hydroxide, and at least one species of compound selected from the group consisting of a niobium compound, titanium compound, tungsten compound and molybdenum compound is added to the coating layer of the cobalt compound while an alkaline electrolytic solution contains lithium hydroxide, and a lithium hydroxide content is not less than 0.6 mol / L and not more than 1.6 mol / L.

As a result, dissolution of the niobium compound, titanium compound, tungsten compound and molybdenum compound, in the alkaline electrolytic solution, can be inhibited and it becomes possible to maintain an excellent electrically conductive network. Consequently, even if recharge/discharge operations are repeated in a high-temperature atmosphere, it is possible to prevent deterioration of conductivity. Hence, an alkaline storage battery excellent in high-temperature cycle life can be provided.

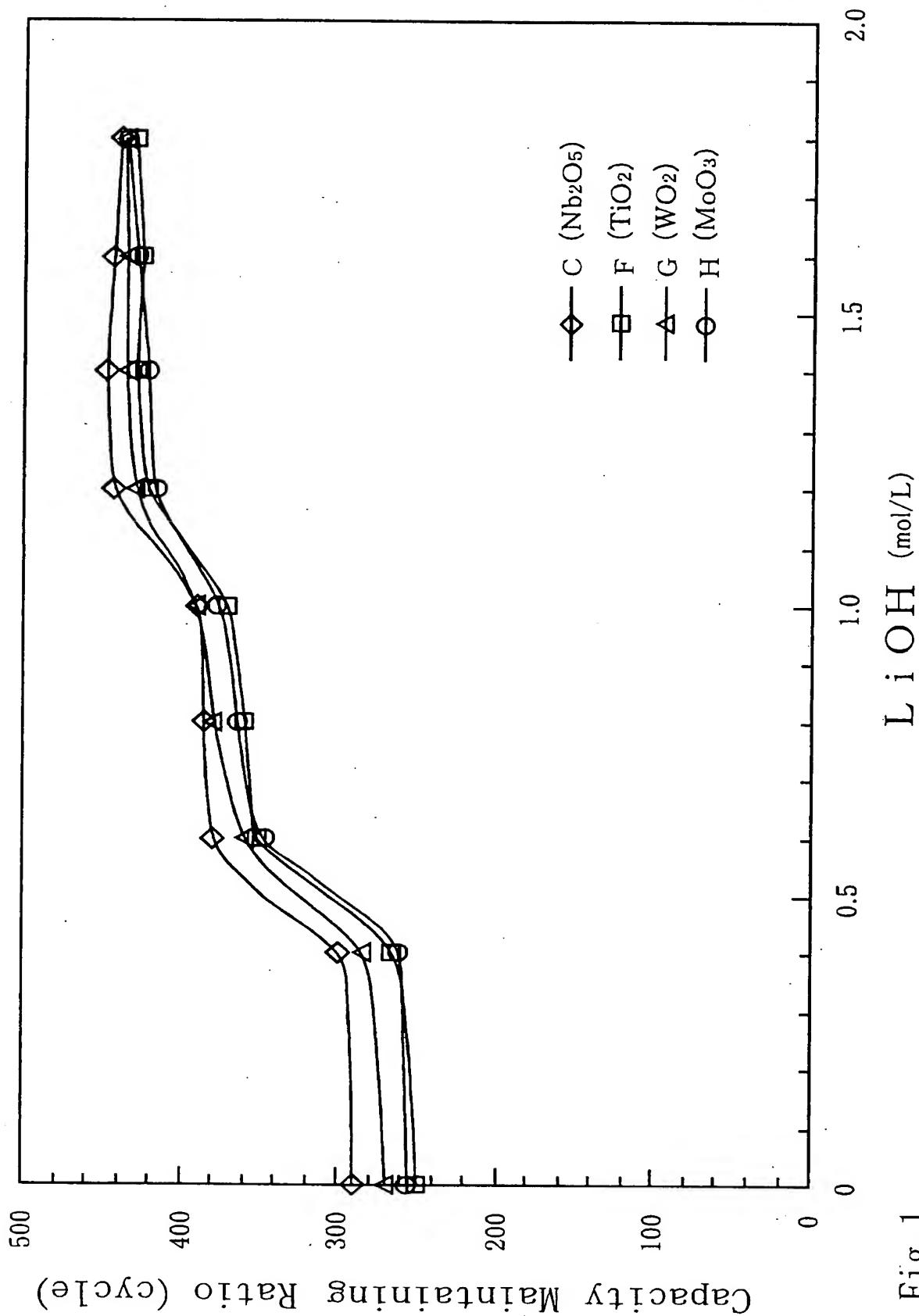


Fig. 1